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14. ABSTRACT
The scope of the present program covers the structure and response of laminar and turbulent premixed and diffusion flames, with emphases on effects of high pressure, flame/flow unsteadiness, and chemistry. Studies on combustion chemistry included: (1) experimental determination of stretch-affected ignition and extinction limits of premixed and nonpremixed flames and the laminar flame speeds for various fuel-oxidizers including CO/H_2, ethylene, 1,3-butadiene, n-heptane, and methyl decanoate; (2) further advances on the method of directed relation graph for mechanism reduction, and auxiliary methodologies for facilitated computation including analytic solution of the quasi-steady species, the lumping of diffusion coefficients, and the development of a fitting formula for the falloff curves of unimolecular reactions; and (3) soot formation in flames through mapping of the toluene flame structure and direct numerical simulations of the turbulent premixed and diffusion flame structure. Studies on flame dynamics show strong coupling between intrinsic flamefront pulsating instability, radiation heat loss, flame stretch, and the extinction limits for diffusion flames, with and without forcing. These accomplishments are expected to be useful to the general interests of AFOSR in the fundamental and practical issues of flame dynamics, chemical kinetics, turbulent combustion, soot formation, radiative hear transfer, flame extinction, and stabilization.

15. SUBJECT TERMS
Laminar flame speeds; ignition temperatures; extinction limits; mechanism reduction; skeletal mechanism; CO/H2 oxidation; ethylene oxidation; heptane oxidation; directed relation graph; high-pressure combustion, pulsating instability, soot formation.

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PHYSICAL AND CHEMICAL PROCESSES IN FLAMES

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SUMMARY/OVERVIEW

The scope of the present program covers the structure and response of laminar and turbulent premixed and nonpremixed flames, with emphases on effects of high pressure, flame/flow unsteadiness, and chemistry. The investigations were conducted through laser-based experimentation, computational simulation with detailed chemistry and transport descriptions, and advanced mathematical analysis. Phenomena studied include the development and control of intrinsic flamefront instabilities, the acquisition of fundamental flame data of high fidelity, and the development of detailed and simplified chemical kinetic mechanisms.

Studies on combustion chemistry proceeded in three directions. In the first, stretch-affected ignition and extinction limits of premixed and nonpremixed flames and laminar flame speeds were determined experimentally for various fuel-oxidizer systems, including those of CO/H_2, ethylene, 1,3-butadiene, n-heptane, and methyl decanoate, allowing scrutiny and improvement of the existing reaction mechanisms. Second, further advances were made on the method of directed relation graph for mechanism reduction and auxiliary methodologies for facilitated computation, including identification of analytic solution of the quasi-steady species, the lumping of diffusion coefficients, and the development of an accurate and computationally simple fitting formula for the falloff curves of unimolecular reactions. Third, soot formation in flames was studied through mapping of the toluene flame structure and direct numerical simulations of the turbulent premixed and nonpremixed flame structure.

Studies on flame dynamics show strong coupling between the intrinsic flamefront pulsating instability, radiation heat loss, flame stretch, and the extinction limits for nonpremixed flames. The influence of forcing leading to resonance and system runaway also was identified and quantified.

Several review articles were written for high-pressure combustion, for the combustion of CO/H_2 mixtures relevant for the utilization of natural gas, for the state and prospect of combustion research, and for mechanism reduction and facilitated computation.

These accomplishments are expected to be useful to the general interests of AFOSR in the fundamental and practical issues of flame dynamics and chemical kinetics, turbulent combustion, soot formation, radiative hear transfer, flame extinction, stabilization, flammability, and supersonic combustion.

ACCOMPLISHMENTS

The scope of the present program, as indicated by its title, is rather broad, covering the chemical kinetics and flame dynamics of combustion processes of interest to aeropropulsion. The study is supported by separate and synergistic investigations involving theory, experiment, and computation. Good progress has been made in a diverse range of phenomena, resulting in 29 journal papers, 21 meeting papers, 8 keynote and named lectures, and 13 invited departmental seminars and session lectures. Highlights of the accomplishments can be found in the annual reports submitted to the program manager, as well as the journal and meeting papers. Thus, only a brief summary of these works is given in the following.

Ignition, Extinction, Laminar Flame Speeds, and Combustion Kinetics

Chemical kinetics and transport-supplemented fluid mechanics form the two knowledge bases of combustion. Traditionally, chemical kinetics has been studied in homogeneous systems such as the shock tube and flow reactors; however, since the early 1980s the usefulness of supplementing results from these homogeneous systems with those from diffusion-affected chemical systems has been recognized. Notable global combustion parameters that have assumed essential roles in the development of reaction mechanisms include the laminar burning velocities and the counterflow extinction strain rates for high-temperature kinetics and the counterflow ignition temperatures for low- to intermediate-temperature kinetics. A major focus of our program is the experimental determination of these kinetically-affected parameters, especially at elevated pressures and using them to scrutinize and aid in the development of detailed reaction mechanisms. During the program period we have made useful contributions in all aspects of such an approach, which are discussed briefly next.

<u>Combustion of the CO/H_2 System</u>

Next to the oxidation of hydrogen, the CO/H_2 system is the foundation fuel constituting the essential building block for hydrocarbon oxidation. The fact that H_2 is required in the oxidation of CO is well established because the crucial reaction pathway is that of $CO+OH\rightarrow CO_2+H$, which produces the key radical H responsible for branching. The alternate reaction $CO+HO_2\rightarrow CO_2+OH$ also becomes important in the presence of excessive HO_2, as in low temperature and/or high pressure situations.

In the first part of this study [1] the kinetics and reactivity associated with the CO + OH and CO + HO_2 reactions were analyzed based on *ab initio* molecular orbital theory, with the interest of identifying the difference in their reaction dynamics that leads to the slower rate of the latter. Two hydrogen-bonded pre-reactive complexes, OOH$\cdots$OC and OOH$\cdots$CO, were found on the potential energy surface of CO + HO_2, having energies that are higher than those of the entrance reactants by 1.2 and 2.9 kcal mol^{-1}, respectively. Through intrinsic reaction coordinate analysis, it was found further that these two complexes hinder the forward reaction, HO_2 + CO $\rightarrow$ products, by forcing a reorientation of the reactants. The configurations of the transition state structures in forming the trans/cis intermediates were rationalized by virtual representation of the electrostatic potentials of the reactants from self-consistent field calculations at the CCSD(T)/AUG-cc-pVTZ level, with the different reactivities of the two reactions ascribed to spatial interactions between the local electrostatic potentials of the entrance reactants. The energy gap of the frontier molecular orbitals for the CO + OH entrance channel was found to be ca. 29 kcal mol^{-1} lower than that of the CO + HO_2 entrance channel by time-dependent coupled cluster theories, which quantitatively explain the difference in their reactivities. Furthermore, the condensed Fukui functions were calculated using Mulliken atomic charges through natural population analysis to identify the most reactive sites of the entrance reactants, with the results again supporting the slower reaction rate of CO + HO_2.

In the second part of this study [2] the laminar flame speeds for CO/H_2/air and CO/H_2/helium mixtures were measured accurately at different equivalence and mixing ratios by the constant pressure spherical flame technique for pressures up to 40 atmospheres. A kinetic mechanism based on recently published, evaluated, and calculated reaction rate constants is presented to model these measured laminar flame speeds, as well as a wide spectrum of other experimental data. The kinetic model accurately predicts our measured flame speeds and the non-premixed counterflow ignition temperatures determined in our previous study, as well as homogeneous system data from literature, such as concentration profiles from flow reactor and ignition delay times from shock tube experiments. This work was presented at the 31st International Combustion Symposium, and published subsequently in the symposium proceedings. Ref. [2] has become one of the most cited papers in that proceeding volume.

Combustion Kinetics of Hydrocarbons

In this series of investigations we studied the combustion kinetics of several hydrocarbon fuels, namely ethylene, 1,3-butadiene, n-heptane, and the biofuel methyl decanoate. Specifically, the atmospheric pressure laminar flame speeds of premixed ethylene/O_2/N_2 mixtures were measured experimentally [3] over equivalence ratios ranging from 0.5 to 1.4 and mixture preheat temperatures varying from 298 to 470 K in the counterflow configuration. Ignition delay measurements also were conducted for ethylene/O_2/N_2/Ar mixtures using a rapid compression machine at compressed pressures from 15 to 50 bar and in the compressed temperature range of 850–1050 K. The experimental laminar flame speeds and ignition delays then were compared to the computed values using two existing chemical kinetic mechanisms. Results show that while the laminar flame speeds are reasonably predicted at room temperature conditions, the discrepancy becomes larger with increasing preheat temperatures. Comparison of experimental and computational ignition delay times also was conducted and discussed. Sensitivity analysis further shows that the ignition delay is highly sensitive to reactions of the vinyl radical with molecular oxygen. The reaction of ethylene with the HO_2 radical was also found to be important for autoignition under the current experimental conditions.

Next [4], the ignition temperatures of nitrogen-diluted 1,3-butadiene by heated air in counterflow were determined experimentally for pressures up to 5 atmospheres and pressure-weighted strain rates from 100 to 250 s^{-1}. The experimental data were compared with computational results using the mechanism of Laskin *et al*. (Laskin, H. Wang and C.K. Law, *Int. J. Chem. Kinet.* 32**,** 589, 2000), showing that, while the overall predication is approximately within the experimental uncertainty, the mechanism over-predicts ignition temperature by about 25 – 40K, with the differences becoming larger in the high pressure/low temperature regime. Sensitivity analyses for the near-ignition states were performed for both reactions and diffusion, which identified the importance of H_2/CO chain reactions, three 1,3-butadiene reaction pathways, and the binary diffusion between 1,3-butadiene and N_2 on ignition. The detailed mechanism, consisting of 94 species and 614 reactions, then was simplified to a skeletal mechanism consisting of 46 species and 297 reactions by using a new reduction algorithm, combining directed relation graph and sensitivity analysis, to be discussed later. The skeletal mechanism was simplified further to a 30-step reduced mechanism by using computational singular perturbation and quasi-steady-state assumptions. Both the skeletal and reduced mechanisms

mimic the performance of the detailed mechanism with good accuracy in both homogeneous and heterogeneous systems.

In the third project [5], laminar flame speeds were determined for *n*-heptane–oxygen–nitrogen mixtures over the pressure range of 0.5 to 2 atm and equivalence ratio range of 0.7 to 1.4 using the counterflow twin-flame technique. For pressure at or below 1.5 atm, the laminar flame speeds were collected for *n*-heptane–air mixtures, whereas the data at 2 atm are reported for diluted air of 18%O_2–82%N_2 composition. These experimental data, together with those acquired previously on the nonpremixed counterflow ignition temperature of *n*-heptane determined over the same range of pressures, were simulated with a high-temperature, detailed kinetic model of *n*-heptane oxidation. After demonstrating satisfactory comparison between the model and experiment, the influence of pressure-induced kinetic effects on the laminar mass flux was analyzed through a computational determination of the overall reaction order. The nonpremixed ignition temperature responses in addition were analyzed by numerical sensitivity analysis on the reaction kinetics and fuel diffusion rate. The influence of uncertainties in the molecular transport on the model prediction of diffusive ignition is discussed.

The fourth project involves the biofuel methyl decanoate [6], for which the detailed chemical kinetic mechanism has been developed and used to study its oxidation. This model was built by following the rules established by Curran *et al.* (H.J. Curran, P. Gaffuri, W.J. Pitz, C.K. Westbrook, *Combustion Flame* 114, 149, 1998) for the oxidation of n-heptane, and it includes all the reactions known to be pertinent to both low and high temperatures. Computed results were compared with methyl decanoate experiments in an engine and oxidation of rapeseed oil methyl esters in a jet stirred reactor. An important feature of this mechanism is its ability to reproduce the early formation of carbon dioxide that is unique to biofuels and due to the presence of the ester group in the reactant. The model also predicts ignition delay times and OH profiles very close to observed values in shock tube experiments fueled by *n*-decane. These model capabilities indicate that large n-alkanes can be good surrogates for large methyl esters and biodiesel fuels to predict overall reactivity, but some kinetic details, including early CO_2 production from biodiesel fuels, can be predicted only by a detailed kinetic mechanism for a true methyl ester fuel. The present methyl decanoate mechanism provides a realistic kinetic tool for the simulation of biodiesel fuels.

The last project [7] deals with the accuracy in the extrapolation of laminar flame speeds from stretch-affected experimental flame speed data. In particular, various factors affecting the determination of laminar flames speeds from outwardly propagating spherical flames in a constant-pressure combustion chamber were considered, with emphasis on the nonlinear variation of the stretched flame speed to the flame stretch rate and the associated need to extrapolate nonlinearly the stretched flame speed to yield accurate determination of the laminar flame speed and Markstein length. Experiments were conducted for lean and rich *n*-butane/air flames, demonstrating the complex and nonlinear nature of the dynamics of flame evolution and the strong influences of the ignition transient and the chamber confinement during the initial and final periods of the flame propagation, respectively. These experimental data were analyzed using the nonlinear relation between the stretched flame speed and stretch rate, yielding laminar flame speeds that agree well with data determined from alternate flame configurations. It is suggested further that the fidelity in the extraction of the laminar flame speed from expanding spherical flames can be facilitated by using small ignition energy and a large combustion chamber.

Mechanism Reduction and Facilitated Computation

Perhaps one of the most significant contributions from the present program in the last funding period is the development of the theory of directed relation graph (DRG) that allows the systematic and accurate reduction of large reaction mechanisms to smaller ones with minimal loss of accuracy. This new theory has been established firmly for the application of reaction mechanisms in computational simulations under two considerations. First, the theory allows the simulation of complex flows such as turbulent flames of small to moderately large hydrocarbons by using realistic chemistry. Second, it allows the simulation of simple flame/flows for complex fuels with extremely large mechanisms characterized by tens of thousands of reactions and thousand of species. Such an advance represents a breakthrough in the computational simulation of chemically-reacting flows. During the program period we have made further contributions towards mechanism reduction. Additionally, we also have identified and developed other avenues for the further reduction of the computation time. These further advances are discussed in the following.

<u>Further Advances in Mechanisms Reduction</u>

In the first study [8] the conditions for application of the directed relation graph (DRG) method in skeletal reduction of mechanisms with vastly different time scales were analyzed systematically. It was found that the existence of quasi-steady state species induces no additional restriction to the application of DRG. When there are partial equilibrium reactions, DRG requires reactions with fast forward or backward rates to be reversible and the backward rate to be computed through the equilibrium constant. The effect of loss in significant digits in the evaluation of species relations due to substantial cancellation between the forward and backward rates of partial equilibrium reactions was identified, and a criterion for minimum accuracy in sampled reaction states for DRG reduction was identified. The method of DRG was then compared with two methods recently developed for skeletal reduction, one based on computational singular perturbation (CSP) and the other is the directed relation graph with error propagation (DRGEP). Advantages and restrictions of including fast-slow subspace separation in skeletal reduction and the validity of the geometric error propagation model in DRGEP were discussed, with examples in existence of exhausted fast processes.

In addition to DRG, another key component for mechanism reduction is lumping, utilizing the concepts of either quasi-steady state (QSS) species or partial equilibrium (PE) reactions. It is, however, not always easy to identify these entities. In this study [9] a criterion based on Computational Singular Perturbation (CSP) is proposed to distinguish the QSS from the fast species induced by reactions in partial equilibrium effectively. Together with DRG, this criteron was applied to the reduction of GRI-Mech 3.0 for methane oxidation, leading to the development of a 19-species reduced mechanism with 15 lumped steps, with the concentrations of the QSS species solved analytically for maximum computational efficiency. Compared to the 12-step and 16-species augmented reduced mechanism previously developed by us, three species, namely O, CH_3OH, and CH_2CO, now are excluded from the QSS species list. The reduced mechanism was validated with a variety of phenomena including perfectly stirred reactors, auto-ignition, and premixed and nonpremixed flames, with the worst-case error being less than 10% over a wide range of parameters. This mechanism then was supplemented with the reactions involving NO formation, followed by validations in both homogeneous and diffusive systems.

Combining the methods of DRG and CSP, a 55-species reduced mechanism for *n*-heptane oxidation subsequently was derived from a detailed mechanism for *n*-heptane that consists of 561 species. This reduced mechanism was derived by first obtaining a skeletal

mechanism with 78 species using DRG aided sensitivity analysis. The unimportant reactions were eliminated by the importance index defined in CSP, with a newly posited restriction to treat each reversible reaction as a single reaction. An isomer lumping approach, also was developed in the present study, then groups the isomers with similar thermal and diffusion properties such that the number of species transport equations is reduced. It was found that the intra-group mass fractions of the isomers could be approximated as constants in the present reduced mechanism, such that a 68-species mechanism with 283 elementary reactions was obtained. Finally, thirteen global QSS species were identified using a CSP-based time scale analysis, resulting in the 55-species reduced mechanism with 283 elementary reactions lumped to 51 semi-global steps. Validation of the reduced mechanism shows good agreement with the detailed mechanism for both ignition and extinction phenomena. The inadequacy of the detailed mechanism in predicting the experimental laminar flame speed also was demonstrated.

A systematic approach [11] also was developed to derive non-stiff reduced mechanisms for direct numerical simulations (DNS) with explicit integration solvers. The stiffness reduction was achieved through on-the-fly elimination of short time scales induced by QSS species and partial equilibrium (PE) reactions. The sparse algebraic equations resulting from QSS species and PE reaction approximations were utilized such that the efficiency of the dynamic stiffness reduction is high compared to the general methods of time-scale reduction based on Jacobian analysis. Using dimension reduction, a non-stiff reduced mechanism with 52 species mechanism was derived from a detailed mechanism with 561 species. The reduced mechanism first was validated for ignition and extinction applications over the parameter range of equivalence ratios, between 0.5 and 1.5, pressures between 10 and 50 atm, and initial temperature between 700 and 1600 K for ignition, and worst case errors of approximately 30% were observed. The reduced mechanism then was applied in 0-D and 1-D unsteady flows with a fixed integration time step of 10ns. The integration was numerically stable and the error induced by the stiffness removal procedure was small.

Further Strategies in Computation Facilitation

Three additional strategies were developed to facilitate computation. The first [12] involves obtaining analytic solutions for the concentrations of the QSS species in reduced mechanisms. The nonlinear algebraic equations for the QSS species concentrations first were approximated by a set of linear equations, and the linearized quasi steady state approximations

(LQSSA) then were solved analytically with a directed graph, namely a QSSG, which was abstracted from the inter-dependence of QSS species. To obtain analytic solutions of high computational efficiency, the groups of strongly connected QSS species first were identified in the QSSG. The inter group couplings then were resolved by a topological sort, and the inner group couplings were solved with variable elimination by substitution. An efficient algorithm was developed to identify a near-optimal sequence for the variable elimination process. The proposed LQSSA-QSSG method was applied to generate a 16-step reduced mechanism for ethylene/air mixture, and good accuracy and high efficiency were observed in simulations of auto-ignition and perfectly stirred reactors with the reduced mechanism.

The second approach [13] involves bundling species with similar diffusivities into groups. The systematic reduction was formulated as an integer programming problem and solved efficiently with a greedy algorithm. Reduction error was controlled by a user-specified threshold value, and the algorithm was automated fully. The method then was applied to a 20-species reduced mechanism for ethylene and the 188-species skeletal mechanism for *n*-heptane. Nine bundled species groups were identified for ethylene, while reduced models with 19, 9, and 3 diffusive species groups were developed for *n*-heptane in ascending order of reduction errors. Validations of the reduced diffusion models obtained with about 10% reduction error in premixed and nonpremixed flames show good agreement with the detailed model, and the worst case reduction error is close to the user-specified level of 10%. Significant reduction in CPU time was observed in the evaluation of the diffusion terms, while the overall time saving is simulation-dependent due to the existence of other terms, such as the chemical source term, which are not affected by the reduction in the diffusion term.

In the third approach we proposed a fitting formula to approximate the fall-off curves of the pressure- and temperature-dependent unimolecular reaction rate constants. Compared with previous fitting formulas, notably that by Troe (Troe, *J. Ber Bunsen-Ges Phys Chem* 87, 161, 1983), the present expression is free of fitting constants and has the potential to reduce the computation time in its evaluation substantially, because of the mathematical simplicity. Five testing reactions from the VariFlex program package (Georgievskii, Y., Klippenstein, S. J., VaReCoF, Sandia National Laboratories and Argonne National Laboratory, 2006) were used to examine the accuracy of the present formula, showing improved performance as compared with previous expressions.

Dynamics and Control of Laminar and Turbulent Flames

Practical combustion situations frequently involve turbulent flames. Under most conditions chemical reactions take place in narrow regions, constituting the so-called laminar flamelets. These laminar flamelets are subjected to the fluctuating shearing action of the turbulent eddies, and under severe conditions can be extinguished locally. Furthermore, because of the disparity in the diffusivities of the heat and reactants, the flame front can exhibit intrinsic instability in the forms of cellularity and pulsation of the flame surface. Studies on flamefront instability during the program period have assumed two directions, namely theoretical analyses of intrinsic pulsating instability of diffusion flames, with and without radiative heat loss and with and without forcing through resonance and high-level computational simulations of turbulent premixed flame propagation. The following is a synopsis of the results and the understanding gained therein.

Intrinsic Instabilities and Extinction of Diffusion Flames

While it is believed generally that, unlike premixed flames, diffusion flames are stable in response to perturbations to diffusional-thermal imbalances because the reaction is diffusion-controlled, it also is recognized that instabilities could be incited when finite-rate chemistry becomes important near limits of extinction. Indeed, it has been suggested that monitoring the onset of such instabilities could allow the control of flame extinction. In the present series of studies we have first derived the general equations describing the response of counterflow diffusion flames with radiative heat loss and preferential diffusion [15], and then systematically applied to the nonlinear oscillations in flames without and with radiation heat loss [16, 17]. Forced oscillation then was imposed to induce resonance, for flames without and with curvatures [18, 19]. Explicit analytical expressions were derived for the parametric boundaries for flame oscillation, extinction, and runaway.

Structure of Turbulent Methane–Air Flames

We also have performed a direct numerical simulation of a three-dimensional spatially developing turbulent slot-burner Bunsen flame [20]. The simulation is performed for three flow-through times, long enough to achieve statistical stationarity. The turbulence parameters have been chosen such that combustion occurs in the regime of thin reaction zones of premixed combustion. The data is analyzed to study possible influences of turbulence on the structure of

preheat and reaction zones. The results show that the mean thickness of the turbulent flame is greater than the corresponding laminar flame. The effects of flow straining and flame front curvature on the mean flame thickness are quantified through conditional means of the thickness and by examining the balance equation for the evolution of the flame thickness. Finally, conditional mean reaction rates of key species compared to the laminar reaction rate profiles show that there is no significant perturbation of the heat release layer.

Soot Formation in Flames

Studies on soot formation have taken two routes, namely detailed experimental analysis of the structure of toluene flames and computational simulation of its formation in turbulent flames, discussed next.

Experimental Analysis of Toluene Pyrolysis in Flames

This project was performed in collaboration with Professor Fei Qi at the University of Science and Technology in China. The work [21] involved experimentation on toluene pyrolysis (1.24% toluene in argon) at low pressure (1.33 kPa) within the temperature range from 1200 to 1800 K. The pyrolysis process was detected with the tunable synchrotron vacuum ultraviolet (VUV) photoionization and molecular beam mass spectrometry (MBMS). Intermediates up to $C_{16}H_{10}$, containing many radicals and isomers, have been identified from near-threshold measurements of photoionization mass spectra. Furthermore, the mole fraction profiles of the pyrolysis products have been evaluated from temperature scan measurements. Based on the experimental results, it is concluded that the benzyl radical is a dominant primary product of toluene pyrolysis. With increasing temperature, the $C_7H_8 \rightarrow C_6H_5$ reaction becomes important gradually. Furthermore, the decomposition pathways of toluene and the benzyl radical were calculated at the G3MP2B3 theoretical level. The calculated barriers of the decomposition pathways are in good agreement with the initial formation temperatures of species. Based on the mole fractions and formation temperatures of the intermediates, a simple reaction network is presented, and the temperature corresponding to the maximum mole fractions of aromatics formed in toluene pyrolysis is found to be 1600 – 1650 K. At relatively high temperatures, H-abstraction is prevalent, and the mole fraction of C_2H_2 is so high that the various aromatics are formed through the HACA mechanism, which is the primary route to the growth of the aromatics (Law, C.K., *Combustion Physics*, CUP,

2006) The five-member-ring recombination mechanism is indispensable as well due to C_5H_5 being a major intermediate in the toluene pyrolysis.

Simulation of Soot Formation in Turbulent Flames

Two computational simulations were performed for soot formation in turbulent flames, on nonpremixed [22] and premixed [23] flames.

The first project [22] was in collaboration with Dr. Jackie Chen of the Sandia National Laboratories. Direct numerical simulations of a two-dimensional, nonpremixed, sooting ethylene flame were performed to examine the effects of soot-flame interactions and transport in an unsteady configuration. A 15-step, 19-species (with10 QSS species) chemical mechanism was used for gas chemistry, with a two-moment, four-step, semi-empirical soot model. Flame curvature is shown to result in flames that move relative to the fluid, either toward or away from rich soot formation regions, resulting in soot being convected essentially into or away from the flame. These relative motions of flame and soot result in a widespread distribution of soot in the mixture fraction coordinate. In regions where the center of curvature of the flame is in the fuel stream, the flame motion is towards the fuel and soot is located near the flame at high temperature, hence having higher reaction rates and radiative heat fluxes. Soot-flame breakthrough also is observed in these regions. Fluid convection and flame displacement velocity relative to fluid convection are of similar magnitudes, while thermophoretic diffusion is five-to-ten times lower. These results emphasize the importance of both unsteady and multi-dimensional effects on soot formation and transport in turbulent flames.

The second project [23] was in collaboration with Professor Suresh Menon of the Georgia Institute of Technology. A subgrid model for soot dynamics is developed for large-eddy simulation (LES) that uses a method of moments approach with Lagrangian interpolative closure (MOMIC) so that no a priori knowledge of the particles' distribution is required. The soot model is implemented within a subgrid mixing and combustion model so that reaction–diffusion–MOMIC coupling is possible without requiring ad hoc filtering. The model includes the entire process, from the initial phase, when the soot nucleus diameter is much smaller than the mean free path, to the final phase, after coagulation and aggregation, where the soot processes can be considered to be in the continuum regime. Relatively detailed multi species ethylene–air kinetics for gas phase combustion are used here to study the effect of inflow turbulence, the carbon–oxygen (C/O) ratio, and multicomponent species diffusion coefficients on soot production in

turbulent premixed flames. The results show that soot formation occurs when the C/O ratio is above the critical value, in good agreement with past observations. Furthermore, we observe that turbulence increases the collision frequency between the soot particles. As a result, the coagulation rate increases, and the total average surface area of the soot particles per unit volume decreases. In addition, the rate of surface growth decreases with the increase in the turbulence intensity. Finally, the inclusion of species transport properties is shown to affect the general structure of the flame in the form of wider curvature probability density function tails and higher turbulent flame speed. In addition, the effect on the thermal diffusivity relative to the molecular diffusivity at the subgrid level changes the surface growth rate and the soot production level.

Review Articles

Four review articles were written on various general issues on combustion, with most of the understanding gained through the present program conducted throughout the years. Reference 26 focuses on high-pressure combustion, while Reference 27 reviews the chemistry and combustion of CO/H_2 mixtures for their relevance to natural gas combustion.

References [28] and [29] are review articles of a massive scale, with the former being the Hottel Lecture at the 31st International Combustion Symposium, and the latter summarizes the state-of-the-art in mechanism reduction as an accounting of what we have accomplished in this important area through the present program.

Writing review articles is a major, time-consuming, though essential, undertaking. The P.I. is pleased to have contributed to the literature in this manner.

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JOURNAL PUBLICATIONS

Flame Speeds, and Ignition, Extinction, Laminar Combustion Kinetics

1. "Chemical reactivity analysis of the CO+OH and CO+HO_2 reactions," by H.Y. Sun and C.K. Law, *J. Molecular Structure: THEOCHEM* 862, 138-147 (2008).
2. "High-pressure laminar flame speeds and kinetic modeling of carbon monoxide/hydrogen combustion," by H.Y. Sun, S.Y. Yang, G. Jomaas, and C.K. Law, *Proc. Combustion Institute* 31, 439-446 (2007).
3. "An experimental investigation on ethylene/O_2/diluent mixtures: laminar flame speeds with preheat and ignition delays at high pressures," K. Kumar, G. Mittal, C. J. Sung and C. K. Law, *Combustion and Flame* 153, 343-354 (2008).
4. "Experimental counterflow ignition temperatures and reaction mechanisms of 1, 3-butadiene," by X.L. Zheng, T.F. Lu, and C. K. Law, *Proceedings of Combustion Institute* 31, 367-375 (2007).
5. "Experimental and modeling study of laminar flame speed and nonpremixed counterflow ignition of n-heptane," A.J. Smallbone, W. Liu, C.K. Law, X.Q. You, and H. Wang, *Proceedings of the Combustion Institute* 32, 1245-1252 (2009).
6. "Experimental and kinetic modeling study of extinction and ignition of methyl decanoate in laminar nonpremixed flows," by K. Seshadri, T. F. Lu, O. Herbinet, S. Humer, U. Niemann, W. J. Pitz and C. K. Law, *Proceedings of Combustion Institute* 32, 1067-1074 (2009).
7. "Nonlinear effects in the extraction of laminar flame speeds from expanding spherical flames," by A. P. Kelley and C. K. Law, *Combustion and Flame* 156, 1844-1851 (2009).

Mechanism Reduction and Facilitated Computation

8. "On the applicability of directed relation graph to the reduction of reaction mechanisms," by T.F. Lu and C.K. Law, *Combustion and Flame* 146, 472-483 (2006).
9. "A CSP-based criterion for the identification of QSS species: A reduced mechanism for methane oxidation with NO chemistry," by T. F. Lu and C. K. Law, *Combustion and Flame* 154, 761-774 (2008).

10. "Strategies for mechanism reduction for large hydrocarbons: n-heptane," by T. F. Lu and C. K. Law, *Combustion and Flame* 154, 153-163 (2008).
11. "Dynamic stiffness removal for direct numerical simulations," by T. F. Lu, C. K. Law and J. H. Chen, *Combustion and Flame* 156, 1542-1551 (2009).
12. "A Systematic approach to obtain analytic solution of quasi steady state species in reduced mechanisms," by T.F. Lu and C.K. Law, *J. Phys. Chem. A*, 110(49), 13202-13208 (2006).
13. "Diffusion coefficient reduction through species bundling," by T.F. Lu and C.K. Law, *Combustion and Flame* 148, 117-126 (2007).
14. "A fitting formula for the falloff curves of unimolecular reactions," by P. Zhang and C.K. Law, *International Journal of Chemical Kinetics* 41, 727-734 (2009).

Dynamics and Control of Laminar and Turbulent Flames

15. "Extinction of counterflow diffusion flames with radiative heat loss and non-unity Lewis numbers," by H.Y. Wang, W.H. Chen, and C.K. Law, *Combustion and Flame* 148, 100-116 (2007).
16. "Nonlinear oscillations in diffusion flames," by H.Y. Wang, J.K. Bechtold, and C.K. Law, *Combustion and Flame* 145, 376-389 (2006).
17. "Oscillation in radiation-affected diffusion flames," by H.Y. Wang and C.K. Law, *Proc. Combustion Institute* 31, 979-987 (2007).
18. "Forced oscillation in diffusion flames near diffusive-thermal resonance," by H.Y. Wang, J.K. Bechtold, and C.K. Law, *International Journal of Heat and Mass Transfer* 51, 630-639, (2008).
19. "Linear response of stretch-affected premixed flames to flow oscillations," by H. Y. Wang, C. K. Law, and T. Lieuwen, *Combustion and Flame* 156, 889-895 (2009).
20. "Structure of a spatially-developing turbulent lean methane-air Bunsen flame," by R. Sankaran, E.R. Hawkes, J.H. Chen, T.F. Lu and C.K. Law, *Proceedings of Combustion Institute* 31, 1291–1298 (2007).

Soot Formation in Flames

21. “An experimental and theoretical study of toluene pyrolysis with tunable synchrotron VUV photoionization and molecular-beam mass spectrometry,” by Taichang Zhang, Lidong Zhang, Xin Hong, Kuiwen Zhang, Fei Qi, Chung K. Law, Taohong Ye, Pinghui Zhao, and Yiliang Chen, *Combustion and Flame* 156, 2071-2083 (2009).
22. “The Effect of Flame Structure on Soot Formation and Transport in Turbulent Nonpremixed Flames Using Direct Numerical Simulation,” by D.O. Lignell, J.H. Chen, P.J. Smith, T.F. Lu, and C.K. Law, *Combustion and Flame* 151, 2–28, (2007).
23. “Simulation of soot formation in turbulent premixed flames,” by H. El-Asrag, T.F. Lu, C.K. Law, and S. Menon, *Combustion and Flame* 150, 108-126 (2007).

Review Articles

24. “Propagation, structure, and limit phenomena of laminar flames at elevated pressures,” by C.K. Law, *Combustion Science and Technology* 178, 335-360 (2006).
25. “Fundamental combustion properties of H_2/CO mixtures: Ignition and flame propagation at elevated pressures,” by C. J. Sung and C. K. Law, *Combustion Science and Technology* 180, 1097-1116 (2008).
26. “Combustion at a crossroads: status and prospects,” by C.K. Law, *Proc. Combustion Institute* 31, 1-29 (2007).
27. “Toward accommodating realistic chemistry in large-scale computations,” by T. F. Lu and C. K. Law, *Progress in Energy and Combustion Science* 35, 192-215 (2009).

PREPRINTS AND REPORTS

1. "Multiple criticality in hydrocarbon ignition," by W. Liu and C. K. Law, AIAA Paper 2007-1425, 45th Aerospace Sciences Meeting, Reno, NV, Jan. 8-11, 2007.

2. "Development of an experimental database and kinetic models for surrogate jet fuels," by M. Colket, T. Edwards, S. Williams, N. Cernansky, D. L. Miller, F. N. Egolfopoulos, P. Lindstedt, K. Seshadri, F. L. Dryer, C. K. Law, D. Friend, D. B. Lenhert, H. Pitsch, A. Sarofim, M. Smooke, and W. Tsang, AIAA Paper 2007-770, 45th Aerospace Sciences Meeting, Reno, NV, Jan. 8-11, 2007.

3. "Development of an experimental database and kinetic models for surrogate diesel fuels," by J. T. Farrell, N. P. Cernansky, F. L. Dryer, D. G. Friend, C. A. Hergart, C. K. Law, R. M. McDavid, C. J. Mueller, A. K. Patel, H. Pitsch, SAE Paper 2007-01-0201, 2007.

4. "Experiments on ethylene/O_2/diluent mixtures: laminar flame speeds with preheat and ignition delays at high pressures," by K. Kumar, G. Mittal, C. J. Sung, and C. K. Law, Paper No. A21, Fifth US Combustion Meeting, San Diego, CA, March 25-28, 2007.

5. "Direct numerical simulations of soot formation and transport in non-premixed turbulent ethylene flames," by D. Lignell, J. H. Chen, P. Smith, T. F. Lu and C. K. Law, Paper No. B01, Fifth US Combustion Meeting, San Diego, CA, March 25-28, 2007.

6. "Direct numerical simulation of stationary lean premixed methane-air flames under intense turbulence," by R .Sankaran, E. R. Hawkes, C. S. Yoo, J. H. Chen, T. F. Lu, and C. K. Law, Paper No. B09, Fifth US Combustion Meeting, San Diego, CA, March 25-28, 2007.

7. "An efficient reduced mechanism for methane oxidation with NOx chemistry," by T. F. Lu and C. K. Law, Paper No. C17, Fifth US Combustion Meeting, San Diego, CA, March 25-28, 2007.

8. "A reduced mechanism for heptane oxidation," by T. F. Lu and C. K. Law, Paper No. C21, Fifth US Combustion Meeting, San Diego, CA, March 25-28, 2007..

9. "Direct numerical simulation of extinction and re-ignition in a nonpremixed turbulent ethylene jet flame," by D. O. Lignell, J. H. Chen, T. F. Lu and C. K. Law, Paper No. 07F-56, Fall Tech. Meeting of the Western States Section Meeting of the Combustion Institute, Sandia National Lab., Livermore, CA, Oct. 16-17, 2007.

10. "Nonlinear effects in the experimental determination of laminar flame properties from stretched flames," A. P. Kelley and C. K. Law, Paper No. B-11, Technical Meeting of the Eastern Section of the Combustion Institute, Charlottesville, VA, Oct. 21-24, 2007.

11. "Towards accommodating realistic fuel chemistry in large-scale computation," by C. K. Law and T. F. Lu, AIAA-2008-0969, 46th Aerospace Sciences Meeting, Reno, NV, Jan. 7-10, 2008. **Invited Paper**.

12. "Development of non-stiff reduced mechanisms for direct numerical simulations," by T. F. Lu and C. K. Law, AIAA-2008-1010, 46th Aerospace Sciences Meeting, Reno, NV, Jan. 7-10, 2008.

13. "Analysis of a turbulent lifted hydrogen/air jet flame from direct numerical simulation with computational singular perturbation," by T. F. Lu, C.S. Yoo, J.H. Chen and C. K. Law, AIAA-2008-1013, 46th Aerospace Sciences Meeting, Reno, NV, Jan. 7-10, 2008.

14. "Experimental determination of the critical radius for spherical flame propagation," by A. P. Kelley, G. Jomaas, and C. K. Law, Paper No. AIAA-2008-1054, 46th Aerospace Sciences Meeting, Reno, NV, Jan. 7-10, 2008.

15. "Experimental measurements of n-pentane flame speeds at elevated pressures and temperatures," by A.P. Kelley, A.J. Smallbone, D.L. Zhu, and C.K. Law, Paper No. 11H4, 6th US National Combustion Meeting, Ann Arbor, MI, May 17-20, 2009.

16. "A fitting formula for pressure and temperature dependence of unimolecular reaction rate constants," by P. Zhang and C.K. Law, Paper No. 13G5, 6th US National Combustion Meeting, Ann Arbor, MI, May 17-20, 2009..

17. "A mode tracking method for flow classification," by T.F. Lu, M.J. Wang, C.S. Yoo, J.H. Chen, and C.K. Law, Paper No. 23D3, 6th US National Combustion Meeting, Ann Arbor, MI, May 17-20, 2009.

18. "Reduced mechanism of iso-octane oxidation," by Y.X. Xin, T.F. Lu, and C.K. Law, 6th US National Combustion Meeting, Ann Arbor, MI, May 17-20, 2009.

19. "Investigation on the intermediate pool of monocyclic aromatic fuels in fuel-rich premixed flames: intermediate identification and mass spectroscopic analysis," by Y.Y. Li, T. Yuan, K.W. Zhang, J.Z. Yang, F. Qi, and C.K. Law, Paper No. 32E2, 6th US National Combustion Meeting, Ann Arbor, MI, May 17-20, 2009.

20. "A fitting formula for the falloff curves of unimolecular reactions with tunneling," by P. Zhang and C.K. Law, Paper No. A-16, Tech. Meeting of the Eastern States Section, the Combustion Institute, University of Maryland, Baltimore, MD, Oct. 18-21, 2009..

21. "Effects of hydrogen addition on spherically expanding n-butane flames," by C.L. Tang, Y.Y. Li, Z.H. Huang, and C.K. Law, Paper No. B-05, Tech. Meeting of the Eastern States Section, the Combustion Institute, University of Maryland, Baltimore, MD, Oct. 18-21, 2009.

PRESENTATIONS

Keynote and Named Lectures

1. "Dynamics of droplet collision," Technical Meeting of the Institute for Liquid Atomization and Spray Systems (ILASS), Chicago, IL, May 15-17, 2007. **Conference Keynote Lecture**

2. "The role of combustion in climate change and energy sustainability," Sixth Asian-Pacific Conference on Combustion, Nagoya, Japan, May 21-23, 2007. **Conference Opening Lecture**

3. "The role of combustion in aerospace and space studies," I.I. Glass Memorial Lecture, University of Toronto Institute for Aerospace Studies, Toronto, Canada, June 7, 2007.

4. "The role of combustion in hydrogen economy," Conference of the Korean Combustion Society, Korea, May 15, 2008. **Conference Keynote Lecture**

5. "The role of combustion and fuels in climate change and energy sustainability," Annual Conference of the Chinese Combustion Society, Xi'an, China, October 25, 2008. **Conference Keynote Lecture**

6. "From atomic to cosmic: a panoramic view of combustion," Ninth Asian-Pacific International Symposium on Combustion and Energy Utilization, Beijing, China, November 3, 2008. **Conference Plenary lecture**

7. "Advancing combustion science through space and aerospace applications: continuing the legacy of G.M. Faeth," Second Gerard M. Faeth Memorial Lecture, Department of Aerospace Engineering, University of Michigan, Ann Arbor, March 12, 2009.

8. "Strategies for mechanism reduction in CFD," 7th Asia-Pacific Conference on Combustion, Taipei, Taiwan, May 25, 2009. **Conference Plenary Lecture**

Invited Departmental Seminars and Conference Session Talks

1. "From atomic to cosmic: A panoramic view of combustion," School of Engineering Open Lecture, Hong Kong Polytechnic University, Hong Kong, April 13, 2007.

2. "Development of computationally accessible reaction mechanisms for simulation of combustion processes," Ford Research Laboratories, Dearborn, MI, Sept. 28, 2007.

3. "Towards accommodating realistic chemistry in large-scale simulations," 46th Aerospace Sciences Meeting, Reno, NV, Jan. 6-10, 2008.

4. “The role of combustion in science and technology,” Department of aerospace Engineering, Korean Advanced Institute of Science and Technology, Daejeon, Korea, May 13, 2008.

5. “Towards accommodating realistic chemistry in large-scale simulations,” Department of Mechanical Engineering, Seoul National University, Seoul, Korea, May 14, 2008.

6. “The role of combustion and fuels in climate change and energy sustainability,” Eighth Emerging Information and Technology Conference, Tainan, Taiwan, June 26, 2008.

7. “The role of combustion in hydrogen economy,” University of Science and Technology of China, Hefei, China, October 27, 2008.

8. “The role of combustion in aerospace and space studies,” Beijing University of Aeronautics and Astronautics, October 29, 2008.

9. “A seminar on combustion,” Institute of Mechanics, Chinese Academy of Sciences, Beijing, China, October 30, 2008.

10. “Clean and efficient combustion for transportation: Research agenda and recent progress,” Tsinghua University, Beijing, China, October 31, 2008.

11. “Dynamics and morphology of expanding spherical flames,” Department of Aerospace Engineering, Purdue University, Feb. 19, 2009.

12. “Dynamics and morphology of expanding spherical flames,” School of Mechanical Engineering, Seoul National University, June 4, 2009.

13. “Advancing combustion science through aerospace applications,” School of Aerospace Engineering, Georgia Institute of Technology, Oct. 22, 2009.

PERSONNEL

Principal Investigator

C.K. Law

Senior Collaborators

J.K. Bechtold (New Jersey Institute of Technology)
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Suresh Menon (Georgia Institute of Technology)
F. Qi (University of Science and Technology of China)
C.J. Sung (University of Connecticut)
H. Wang (University of Southern California)

Post-Doctoral Fellows and Research Staff

T.F. Lu
A.J. Smallbone
H.Y. Sun
D.L. Zhu

Graduate Students

G. Jomaas (Ph.D. student; graduated 2008)
H.Y. Wang (Ph.D. student; graduated 2008)
A.P Kelley
W. Liu
P. Zhang

SIGNIFICANT INTERACTIONS

1. **Contact:** The Dow Chemical Company; Albert Harvey; (225) 353-4035

   Results: Use of comprehensively validated reduced chemical kinetic mechanism allows realistic description of methane oxidation chemistry

   Applications: In-house code development and use.

2. **Contact:** United Technology Research Center; M.D. Colket; (860) 610-7481

   Results: Use of comprehensively validated reduced chemical kinetic mechanism allows realistic description of methane oxidation chemistry

   Applications: In-house code development and use

3. **Contact:** Fluent, Inc.; Graham Goldin; (800) 445-4454

   Results: Use of comprehensively validated reduced chemical kinetic mechanism allows realistic description of methane oxidation with NOx formation

   Applications: Commercially available code for engine and burner simulation

4. **Contact:** Rolls Royce; M. S. Anand, 317- 230-2828

   Results: Use of comprehensively validated reduced chemical kinetic mechanism allows improved description of complex species and velocity fields

   Applications: Realistic simulation of combustors, especially predictions of pollutant Formation

5. **Contact:** Combustion Research and Flow Technologies; S. Arunajatesan, 215-766-1520

   Results: Use of comprehensively validated reduced chemical kinetic mechanism allows realistic description of methane oxidation chemistry with NO_x formation.

   Applications: Realistic simulation of combustors, especially predictions of pollutant formation